

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11)

**EP 0 971 021 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
12.01.2000 Bulletin 2000/02

(51) Int. Cl. 7:

**C11D 3/00, C11D 3/20,  
C11D 3/30, C11D 3/22,  
C11D 3/37, C11D 3/33,  
C11D 3/50, C11D 17/06**

(21) Application number: **99870029.8**

(22) Date of filing: **15.02.1999**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: **10.07.1998 EP 98870156  
28.10.1998 EP 98870227  
10.07.1998 EP 98870155  
28.10.1998 EP 98870226  
11.02.1999 EP 99870026  
11.02.1999 EP 99870025**

(71) Applicant: **THE PROCTER & GAMBLE COMPANY**  
Cincinnati, Ohio 45202 (US)

(72) Inventors:  
, **Busch, Alfred, (NMN)**  
**1840 Londerzeel (BE)**  
, **Homble, Marcel, (NMN)**  
**3060 Bertem (BE)**  
, **Laudamiel, Christophe, (NMN)**  
**1000 Brussels (BE)**  
, **Smets, Johan, (NMN)**  
**3210 Lubbeek (BE)**  
, **Trujillo, Rafael, (NMN)**  
**1410 Waterloo (BE)**  
, **Wevers, Jean, (NMN)**  
**1840 Steenhuffel (BE)**

(74) Representative:  
**Gault, Nathalie et al**  
**BVBA Procter & Gamble Europe Sprl**  
**Temselaan 100**  
**1853 Strombeek-Bever (BE)**

(54) **Process for producing particles of amine reaction product**

(57) There is provided a process for producing particles of amine reaction product by means of a carrier having a melting point between 30°C and 135°C, optionally followed by a coating step. Processed amine reaction products and finished compositions incorporating such processed product are also herein provided.

EP 0 971 021 A1

**Description**Field of the invention

[0001] The present invention relates to a process for producing particles of amine reaction product.

Background of the invention

[0002] Perfumed products are well-known in the art. However, consumer acceptance of such perfumed products like laundry and cleaning products is determined not only by the performance achieved with these products but also by the aesthetics associated therewith. The perfume components are therefore an important aspect of the successful formulation of such commercial products.

[0003] It is also desired by consumers for treated fabrics to maintain the pleasing fragrance over time. Indeed, perfume additives make such compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume carried-over from an aqueous laundry bath onto fabrics is often marginal and does not last long on the fabric. Furthermore, fragrance materials are often very costly and their inefficient use in laundry and cleaning compositions and ineffective delivery to fabrics results in a very high cost to both consumers and laundry and cleaning manufacturers. Industry, therefore, continues to seek with urgency for more efficient and effective fragrance delivery in laundry and cleaning products, especially for improvement in the provision of long-lasting fragrance to the fabrics.

[0004] It has recently been found that an amine reaction product of a compound containing a primary amine functional group and an active ketone or aldehyde containing component fulfills such a need. Disclosure of such compounds can be found in recently filed applications EP 98870227.0, EP 98870226.2, EP 99870026.4, and EP 99870025.6, all incorporated herein by reference.

[0005] However, a problem now encountered with the use of these compound is their ease of incorporation into fully formulated compositions. Indeed, such amine reaction products are often viscous which renders their incorporation into these fully formulated compositions more cumbersome.

[0006] It is therefore an object of the invention to provide amine reaction product in a form suitable for easy incorporation into fully formulated composition.

[0007] It has now been found that the mixing of the amine reaction product with a carrier having specific melting point to form a particle fulfills such a need. Preferably, the obtained particle is thereafter treated to form a coated particle.

[0008] Further, it has also been advantageously found that both viscous and non-viscous amine reaction product when processed by the present invention exhibit better deposition and long lasting release than amine reaction product which have not been processed according to this process. Not to be bound by theory, it is believed that the mixing with such carrier act as a shell around the amine reaction product, thus protecting it from the aggressive wash liquor as well as enhancing its fabric deposition properties.

[0009] By "viscous", it is meant a product which has a viscosity higher than 1000 cps. The viscosity is measured on a rheometer, TA Instrument CSL  $\dot{\gamma}_{100}$  at a temperature of 25°C with a gap setting of 500 microns.

[0010] The carrier for use herein has a melting point, measured at atmospheric pressure, of from 30°C to 135°C.

Summary of the invention

[0011] The present invention is a process for making particles of amine reaction product of a compound containing a primary amine functional group and an active ketone or aldehyde containing component, and which comprises the steps of:

a)-providing the amine reaction product, and

b)-mixing therewith a carrier having a melting point of from 30°C to 135°C.

[0012] In a preferred embodiment of the invention, the obtained particle is further processed to form a coated particle.

Detailed description of the inventionStarting materials

1)-Amine reaction product

[0013] The amine reaction product for use herein is a product of reaction between a compound containing a primary amine functional group and an active ketone or aldehyde containing component, so called hereinafter "amine reaction product".

## EP 0 971 021 A1

[0014] A typical disclosure of amine reaction product suitable for use herein can be found in recently filed applications EP 98870227.0, EP 98870226.2, EP 99870026.4, and EP 99870025.6, all incorporated herein by reference.

### A-Primary amine

[0015] By "primary amine", it is meant a component which carries at least one primary amine and/or amide function.

[0016] Preferably, the primary amine compound is also characterized by an Odour Intensity Index of less than that of a 1% solution of methylantranilate in dipropylene glycol.

### Odour Intensity Index method

[0017] By Odour Intensity Index, it meant that the pure chemicals were diluted at 1% in Dipropylene Glycol, odor-free solvent used in perfumery. This percentage is more representative of usage levels. Smelling strips, or so called "blotters", were dipped and presented to the expert panellist for evaluation. Expert panellists are assessors trained for at least six months in odor grading and whose gradings are checked for accuracy and reproducibility versus a reference on an on-going basis. For each amine compound, the panellist was presented two blotters: one reference (Me Anthranilate, unknown from the panellist) and the sample. The panellist was asked to rank both smelling strips on the 0-5 odor intensity scale, 0 being no odor detected, 5 being very strong odor present.

### Results:

[0018] The following represents Odour Intensity Index of an amine compound suitable for use in the present invention and according to the above procedure. In each case, numbers are arithmetic averages among 5 expert panellists and the results are statistically significantly different at 95% confidence level:

Methylantranilate 1% (reference)	3.4
Ethyl-4-aminobenzoate (EAB) 1%	0.9

[0019] A general structure for the primary amine compound of the invention is as follows:



wherein B is a carrier material, and n is an index of value of at least 1.

[0020] Preferred B carriers are inorganic or organic carriers.

[0021] By "inorganic carrier", it is meant carrier which are non-or substantially non carbon based backbones.

[0022] Preferred primary amines, among the inorganic carriers, are those selected from mono or polymers or organic-organosilicon copolymers of amino derivatised organo silane, siloxane, silazane, alumane, aluminum siloxane, or aluminum silicate compounds. Typical examples of such carriers are: organosiloxanes with at least one primary amine moiety like the diaminoalkylsiloxane  $[H_2NCH_2(CH_3)_2Si]_nO$ , or the organoaminosilane  $(C_6H_5)_3SiNH_2$  described in: Chemistry and Technology of Silicone, W. Noll, Academic Press Inc. 1998, London, pp 209, 106).

[0023] Preferred primary amines, among the organic carriers, are those selected from aminoaryl derivatives, polyamines, amino acids and derivatives thereof, substituted amines and amides, glucamines, dendrimers, the polyvinylamines with a MW of from 600-50K; amino substituted polyvinylalcohol with a MW ranging from 400-300,000; polyoxyethylene bis [amine]; polyoxyethylene bis [6-aminoethyl]; N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched; 1,4-bis-(3-aminopropyl) piperazine, and mixtures thereof.

[0024] Preferred aminoaryl derivatives are the amino-benzene derivatives including the alkyl esters of 4-amino benzoate compounds, and more preferably selected from ethyl-4-amino benzoate, phenylethyl-4-aminobenzoate, phenyl-4-aminobenzoate, 4-amino-N'-(3-aminopropyl)-benzamide, and mixtures thereof.

[0025] Polyamines suitable for use in the present invention are polyethyleneimines polymers, poly[oxy(methyl-1,2-ethanediyl)],  $\alpha$ -(2-aminomethylethyl)- $\omega$ -(2-aminomethyl-ethoxy)- (= C.A.S No. 9046-10-0); poly[oxy(methyl-1,2-ethanediyl)],  $\alpha$ -hyd ro)- $\omega$ -(2-aminomethylethoxy)-, ether with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (= C.A.S. No. 39423-51-3); commercially available under the tradename Jeffamines T-403, D-230, D-400, D-2000; 2,2',2"-triaminotriethylamine; 2,2'-diamino-diethylamine; 3,3'-diamino-dipropylamine, 1,3 bis aminoethyl-cyclohexane commercially available from Mitsubushi and the C12 Sternamines commercially available from Clariant like the C12 Sternamin(propylenamine)<sub>n</sub> with n=3/4, and mixtures thereof. Preferred polyamines are polyethyleneimines commercially available under the tradename Lupasol like Lupasol FG, G20,wfv, PR8515, WF, FC, G20, G35, G100, HF, P, PS, SK, SNA.

[0026] Preferred amino acids for use herein are selected tyrosine, tryptophane, lysine, glutamic acid, glutamine, aspartic acid, arginine, asparagine, phenylalanine, proline, glycine, serine, histidine, threonine, methionine, and

## EP 0 971 021 A1

mixture thereof, most preferably selected from tyrosine, tryptophane, and mixture thereof. Preferred amino acid derivatives selected from tyrosine ethylate, glycine methylate, tryptophane ethylate, and mixture thereof.

[0027] Preferred substituted amines and amides for use herein are selected from nipecotamide, N-coco-1,3-propanediamine; N-oleyl-1,3-propanediamine; N-(tallow alkyl)-1,3-propanediamine; 1,4-diamino cyclohexane; 1,2-diamino-cyclohexane; 1,12-diaminododecane, and mixtures thereof.

[0028] Other primary amine compounds suitable for use herein are the glucamines, preferably selected from 2,3,4,5,6-pentamethoxy-glucamine; 6-acetylglucamine, glucamine, and mixture thereof.

[0029] Also preferred compounds are the polyethylenimine and/or polypropylenimine dendrimers and the commercially available Starburst® polyamidoamines (PAMAM) dendrimers, generation G0-G10 from Dendritech and the dendrimers Astromols®, generation 1-5 from DSM being DiAminoButane PolyAmine DAB (PA)<sub>x</sub> dendrimers with  $x = 2^n$  and  $n$  being generally comprised between 0 and 4.

[0030] Still other preferred primary amine compounds are :

- polyvinylamines with a molecular weight (MW) ranging from 600, 1200, 3K, 20K, 25K or 50K;
- amino substituted polyvinylalcohol with a MW ranging from 400-300,000;
- polyoxyethylene bis [amine] available from e.g. Sigma;
- polyoxyethylene bis [6-aminoethyl] available from e.g. Sigma;
- N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched (TPTA)
- 1,4-bis-(3-aminopropyl) piperazine (BNPP).

[0031] The more preferred compounds are ethyl-4-amino benzoate, polyethyleneimine polymers commercially available under the tradename Lupasol like Lupasol FG, G20,wfv, PR8515, WF, FC, G20, G35, G100, HF, P, PS, SK, SNA; glucamine; the diaminobutane dendrimers Astramol®, polyvinylamines with a MW ranging from 600, 1200, 3K, 20K, 25K or 50K; amino substituted polyvinylalcohol with a MW ranging from 400-300,000; polyoxyethylene bis [amine]; polyoxyethylene bis [6-aminoethyl]; N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched; 1,4-bis-(3-aminopropyl) piperazine, and mixture thereof. Most preferred primary amine compounds are selected from ethyl-4-amino benzoate, polyethyleneimine polymers commercially available under the tradename Lupasol like Lupasol FG, G20,wfv, PR8515, WF, FC, G20, G35, G100, HF, P, PS, SK, SNA; the diaminobutane dendrimers Astramol®, N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched; 1,4-bis-(3-aminopropyl) piperazine, and mixtures thereof. Even most preferred compounds are those selected from ethyl-4-amino benzoate, polyethyleneimine polymers commercially available under the tradename Lupasol like Lupasol FG, G20,wfv, PR8515, WF, FC, G20, G35, G100, HF, P, PS, SK, SNA; N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched, 1,4-bis-(3-aminopropyl) piperazine, and mixtures thereof.

[0032] Advantageously, such most preferred primary amine compounds also provide fabric appearance benefit, in particular colour appearance benefit, thus providing a resulting amine reaction product with the dual properties of both fabric appearance benefit and delayed release of the active. Further, when the primary amine compound has more than one free primary amine group, several different active ingredients (aldehyde and/or ketone) can be linked to the amine compound.

### B-Active ketone and/or aldehyde

[0033] Preferably, for the above mentioned compounds, by active ketone or active aldehyde, it is meant any chain containing at least 1 carbon atom, preferably at least 5 carbon atoms.

[0034] Preferably, the active ketone or active aldehyde is respectively selected from a flavour ketone or aldehyde ingredient, a pharmaceutical ketone or aldehyde active, a biocontrol ketone or aldehyde agent, a perfume ketone or aldehyde component and mixtures thereof, most preferably a perfume ketone and/or aldehyde.

[0035] Flavour ingredients include spices, flavor enhancers that contribute to the overall flavour perception.

[0036] Pharmaceutical actives include drugs.

[0037] Biocontrol agents include biocides, antimicrobials, bactericides, fungicides, algacides, mildewcides, disinfectants, antiseptics, insecticides, vermicides, plant growth hormones.

[0038] A typical disclosure of suitable ketone and/or aldehydes, traditionally used in perfumery, can be found in "perfume and Flavor Chemicals", Vol. I and II, S. Arctander, Allured Publishing, 1994, ISBN 0-931710-35-5.

[0039] Perfume ketones components include components having odoriferous properties.

[0040] Preferably, for the above mentioned compounds, the perfume ketone is selected from buccoxime; iso jasmone; methyl beta naphthyl ketone; musk indanone; tonalid/musk plus; Alpha-Damascone, Beta-Damascone, Delta-Damascone, Iso-Damascone, Damascenone, Damarose, Methyl-Dihydrojasmonate, Menthone, Carvone, Camphor, Fenchone, Alpha-Ionone, Beta-Ionone, Gamma-Methyl so-called Ionone, Fleuramone, Dihydrojasmone, Cis-Jasmone, Iso-E-Super, Methyl-Cedrenyl-ketone or Methyl-Cedrylone, Acetophenone, Methyl-Acetophenone, Para-Methoxy-Acetophenone, Methyl-Beta-Naphtyl-Ketone, Benzyl-Acetone, Benzophenone, Para-Hydroxy-Phenyl-

Butanone, Celery Ketone or Livescone, 6-Isopropyldecahydro-2-naphtone, Dimethyl-Octenone, Freskomenthe, 4-(1-Ethoxyvinyl)-3,3,5,5-tetramethyl-Cyclohexanone, Methyl-Heptenone, 2-(2-(4-Methyl-3-cyclohexen-1-yl)propyl)-cyclopentanone, 1-(p-Menthen-6(2)-yl)-1-propanone, 4-(4-Hydroxy-3-methoxyphenyl)-2-butanone, 2-Acetyl-3,3-Dimethyl-Norbornane, 6,7-Dihydro-1,1,2,3,3-Pentamethyl-4(5H)-Indanone, 4-Damascol, Dulcinyol or Cassione, Gelsone, Hexalon, Isocyclemon E, Methyl Cyclocitronone, Methyl-Lavender-Ketone, Orivon, Para-tertiary-Butyl-Cyclohexanone, Verdone, Delphone, Muscone, Neobutenone, Plicatone, Veloutone, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Tetrameran, hedione, and mixtures thereof.

**[0041]** More preferably, for the above mentioned compounds, the preferred ketones are selected from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-Ionone, Iso-E-Super, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, hedione, and mixtures thereof.

**[0042]** Perfume aldehyde components include components having odoriferous properties.

**[0043]** Preferably, for the above mentioned compounds, the perfume aldehyde is selected from adoxal; anisic aldehyde; cymal; ethyl vanillin; florhydral; helional; heliotropin; hydroxycitronellal; koavone; lauric aldehyde; lyral; methyl nonyl acetaldehyde; P. T. buccinal; phenyl acetaldehyde; undecylenic aldehyde; vanillin; 2,6,10-trimethyl-9-undecenal, 3-dodecen-1-al, alpha-n-amylic cinnamic aldehyde, 4-methoxybenzaldehyde, benzaldehyde, 3-(4-tert-butylphenyl)-propanal, 2-methyl-3-(para-methoxyphenyl) propanal, 2-methyl-4-(2,6,6-trimethyl-2(1)-cyclohexen-1-yl) butanal, 3-phenyl-2-propanal, cis-/trans-3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-6-octen-1-al, [(3,7-dimethyl-6-octenyl)oxy] acetaldehyde, 4-isopropylbenzaldehyde, 1,2,3,4,5,6,7,8-octahydro-8,8-dimethyl-2-naphthaldehyde, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, 2-methyl-3-(isopropylphenyl)propanal, 1-decanal; decyl aldehyde, 2,6-dimethyl-5-heptenal, 4-(tricyclo[5.2.1.0(2,6)]-decylidene-8)-butanal, octahydro-4,7-methano-1 H-indenecarboxaldehyde, 3-ethoxy-4-hydroxy benzaldehyde, para-ethyl-alpha, alpha-dimethyl hydrocinnamaldehyde, alpha-methyl-3,4-(methylenedioxy)-hydrocinnamaldehyde, 3,4-methylenedioxybenzaldehyde, alpha-n-hexyl cinnamic aldehyde, m-cymene-7-carboxaldehyde, alpha-methyl phenyl acetaldehyde, 7-hydroxy-3,7-dimethyl octanal, Undecenal, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde, 4-(3)(4-methyl-3-pentenyl)-3-cyclohexen-carboxaldehyde, 1-dodecanal, 2,4-dimethyl cyclohexene-3-carboxaldehyde, 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde, 7-methoxy-3,7-dimethyloctan-1-al, 2-methyl undecanal, 2-methyl decanal, 1-nonanal, 1-octanal, 2,6,10-trimethyl-5,9-undecadienal, 2-methyl-3-(4-tertbutyl)propanal, dihydrocinnamic aldehyde, 1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carboxaldehyde, 5 or 6 methoxyhexahydro-4,7-methanoindan-1 or 2-carboxaldehyde, 3,7-dimethyloctan-1-al, 1-undecanal, 10-undecen-1-al, 4-hydroxy-3-methoxy benzaldehyde, 1-methyl-3-(4-methylpentyl)-3-cyclohexenecarboxaldehyde, 7-hydroxy-3,7-dimethyl-octanal, trans-4-decenal, 2,6-nonadienal, para-tolylacetaldehyde, 4-methylphenylacetaldehyde, 2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butenal, ortho-methoxycinnamic aldehyde, 3,5,6-trimethyl-3-cyclohexene carboxaldehyde, 3,7-dimethyl-2-methylene-6-octenal, phenoxyacetaldehyde, 5,9-dimethyl-4,8-decadienal, peony aldehyde (6,10-dimethyl-3-oxa-5,9-undecadien-1-al), hexahydro-4,7-methanoindan-1-carboxaldehyde, 2-methyl octanal, alpha-methyl-4-(1-methyl ethyl) benzene acetaldehyde, 6,6-dimethyl-2-norpinene-2-propionaldehyde, para methyl phenoxy acetaldehyde, 2-methyl-3-phenyl-2-propen-1-al, 3,5,5-trimethyl hexanal, Hexahydro-8,8-dimethyl-2-naphthaldehyde, 3-propyl-bicyclo[2.2.1]-hept-5-ene-2-carbaldehyde, 9-decenal, 3-methyl-5-phenyl-1-pentanal, methylnonyl acetaldehyde, 1-p-menthene-q-carboxaldehyde, citral, linal and mixtures thereof.

**[0044]** Most preferred aldehydes are selected from citral, 1-decanal, benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadienal; alpha-n-amylic cinnamic aldehyde, alpha-n-hexyl cinnamic aldehyde, P.T. Buccinal, lyral, cymal, methyl nonyl acetaldehyde, trans-2-nonenal, linal, trans-2-nonenal, and mixture thereof.

**[0045]** In the above list of perfume ingredients, some are commercial names conventionally known to one skilled in the art, and also includes isomers. Such isomers are also suitable for use in the present invention.

**[0046]** In another embodiment, especially suitable for the purpose of the present invention are the perfume compounds, preferably the perfume ketones or aldehydes, characterised by having a low Odor Detection Threshold. Such Odor Detection Threshold (ODT) should be lower than 1ppm, preferably lower than 10ppb - measured at controlled Gas Chromatography (GC) conditions such as described here below. This parameter refers to the value commonly used in the perfumery arts and which is the lowest concentration at which significant detection takes place that some odorous material is present. Please refer for example in "Compilation of Odor and Taste Threshold Value Data (ASTM DS 48 A)", edited by F. A. Fazzalari, International Business Machines, Hopwell Junction, NY and in Calkin et al., Perfumery, Practice and Principles, John Wiley & Sons, Inc., page 243 et seq (1994). For the purpose of the present invention, the Odor Detection Threshold is measured according to the following method :

The gas chromatograph is characterized to determine the exact volume of material injected by the syringe, the precise split ratio, and the hydrocarbon response using a hydrocarbon standard of known concentration and chain-length distribution. The air flow rate is accurately measured and, assuming the duration of a human inhalation to last 0.02 minutes, the sampled volume is calculated. Since the precise concentration at the detector at any point in time is known, the mass per volume inhaled is known and hence the concentration of material. To determine the ODT of a perfume material, solutions are delivered to the sniff port at the back-calculated concentration. A panelist sniffs the GC effluent and identifies the retention time when odor is noticed. The average over all panelists determines the threshold of noticeability. The necessary amount of analyte is injected onto the column to achieve a certain concentration, such as 10 ppb, at the detector. Typical gas chromatograph parameters for determining odor detection thresholds are listed below.

GC: 5890 Series II with FID detector

7673 Autosampler

Column: J&W Scientific DB-1

Length 30 meters ID 0.25 mm film thickness 1 micron

Method:

Split Injection: 17/1 split ratio

Autosampler: 1.13 microliters per injection

Column Flow: 1.10 mL/minute

Air Flow: 345 mL/minute

Inlet Temp. 245°C

Detector Temp. 285°C

Temperature Information

Initial Temperature: 50°C

Rate: 5C/minute

Final Temperature: 280°C

Final Time: 6 minutes

Leading assumptions: 0.02 minutes per sniff

GC air adds to sample dilution

**[0047]** Examples of such preferred perfume components are those selected from : 2-methyl-2-(para-isopropylphenyl)-propionaldehyde, 1-(2,6,6-trimethyl-2-cyclohexan-1-yl)-2-buten-1-one and/or para-methoxyacetophenone. Even more preferred are the following compounds having an ODT  $\leq 10$ ppb measured with the method described above : undecylenic aldehyde, undecalactone gamma, heliotropin, dodecalactone gamma, p-anisic aldehyde, para hydroxy-phenyl-butanone, cymal, benzyl acetone, ionone alpha, p.t.bucinal, damascenone, ionone beta and methylnonyl ketone.

**[0048]** Typically the level of active is of from 10 to 90%, preferably from 30 to 85%, more preferably from 45 to 80% by weight of the amine reaction product.

**[0049]** Preferred amine reaction products are those resulting from the reaction of polyethyleneimine polymer like Lupasol polymers, BNPP, or TPTA with one or more of the following Alpha Damascone, Delta Damascone, Carvone, Gamma-Methyl-Ionone and 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde. Still other preferred amine reaction products are those resulting from the reaction of Astramol Dendrimers with Carvone as well as those resulting from the reaction of ethyl-4-amino benzoate with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde.

**[0050]** Most preferred amine reaction products are those from the reaction of Lupasol HF with Delta Damascone; LupasolG35 with Alpha Damascone; LupasolG100 with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, BNPP or TPTA with Alpha and Delta Damascone; ethyl-4-amino benzoate with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde.

2)-Carrier

**[0051]** Another essential ingredient of the process invention is a carrier having a melting point between 30°C and 135°C, preferably between 45°C and 85°C. By means of this carrier, particles of amine reaction product will be produced.

**[0052]** Suitable carrier for use in the process invention are components like organic polymeric compounds, waxes, paraffins, oils, glycerides, monoglycerides, diglycerides, triglycerides, anionic surfactants; nonionic surfactants, cationic surfactants, zwitterionic surfactants, and mixtures thereof, preferably selected from organic polymeric compound, nonionic surfactants, and mixtures thereof.

**[0053]** Preferred organic polymeric compounds suitable for mixing with primary amine compound herein include polyethylene glycols, and derivatives thereof, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

## EP 0 971 021 A1

[0054] Essentially any nonionic surfactants useful for deterative purposes can be included in the compositions provided it has a melting point between 30°C and 135°C.

[0055] Exemplary, non-limiting classes of useful nonionic surfactants are listed below.

### Nonionic polyhydroxy fatty acid amide surfactant

[0056] Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula  $R_2CONR_1Z$  wherein:  $R_1$  is H,  $C_1$ - $C_4$  hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably  $C_1$ - $C_4$  alkyl, more preferably  $C_1$  or  $C_2$  alkyl, most preferably  $C_1$  alkyl (i.e., methyl); and  $R_2$  is a  $C_5$ - $C_{31}$  hydrocarbyl, preferably straight-chain  $C_5$ - $C_{19}$  alkyl or alkenyl, more preferably straight-chain  $C_9$ - $C_{17}$  alkyl or alkenyl, most preferably straight-chain  $C_{11}$ - $C_{17}$  alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

### Nonionic condensates of alkyl phenols

[0057] The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 18 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide with from about 1 to about 150 moles of alkylene oxide per mole of alcohol.

### Nonionic ethoxylated alcohol surfactant

[0058] The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 150 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 25 to about 150 moles of ethylene oxide per mole of alcohol, preferably 50 to 100, more preferably 80 moles of ethylene oxide per mole of alcohol.

[0059] Preferred nonionic ethoxylated alcohol surfactants are selected from tallow ( $C_{16}$ - $C_{18}$ ) alcohol ethoxylated with 25, 50, 80, or 100 moles of ethylene oxide commercially available from under the tradename of Lutensol from BASF, Empilan from Albright and Wilson, and Genapol from Clariant. The most preferred nonionic ethoxylated alcohol surfactant is tallow ( $C_{16}$ - $C_{18}$ ) alcohol ethoxylated with 80 moles of ethylene oxide and commercially available under the tradename of Lutensol 80/80 from BASF, Empilan KM 80 from Albright and Wilson, or Genapol T800 from Clariant.

### Nonionic ethoxylated/propoxylated fatty alcohol surfactant

[0060] The ethoxylated  $C_6$ - $C_{22}$  fatty alcohols and  $C_6$ - $C_{22}$  mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the  $C_{10}$ - $C_{22}$  ethoxylated fatty alcohols with a degree of ethoxylation of from 25 to 150, most preferably these are the  $C_{12}$ - $C_{18}$  ethoxylated fatty alcohols with a degree of ethoxylation from 50 to 80. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 30.

### Nonionic EO/PO condensates with propylene glycol

[0061] The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available Pluronic<sup>TM</sup> surfactants, marketed by BASF.

### Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

[0062] The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic<sup>TM</sup> compounds, marketed by BASF.

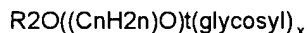
### Nonionic alkylpolysaccharide surfactant

[0063] Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from

## EP 0 971 021 A1

about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

[0064] The preferred alkylpolyglycosides have the formula



wherein  $R_2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms;  $n$  is 2 or 3;  $t$  is from 0 to 10, preferably 0, and  $x$  is from 1.3 to 8, preferably from 1.3 to 3, most preferably from 1.3 to 2.7. The glycosyl is preferably derived from glucose.

### Nonionic fatty acid amide surfactant

[0065] Fatty acid amide surfactants suitable for use herein are those having the formula:  $R^6_aCON(R^7_a)_2$  wherein  $R^6_a$  is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each  $R^7_a$  is selected from the group consisting of hydrogen,  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl, and  $-(C_2H_4O)_xH$ , where  $x$  is in the range of from 1 to 3.

[0066] Preferred carrier materials are selected from nonionic ethoxylated alcohol surfactants.

[0067] Typically when the amine reaction product is only mixed with a carrier but not further processed, the amine reaction product will be present in an amount of from 1 to 75%, preferably 10 to 60%, more preferably 15 to 45% by weight of the processed reaction product in the produced particle. In this instance, the amount of carrier will be sufficient to add up to 100%. Of course, the particle may also contain minors but in quantities which will not exceed the amount of carrier material. Typically the carrier will be present in an amount of from 3 to 95%, preferably from 15 to 80% and most preferably from 25 to 75%, by weight of the produced particles in the processed amine reaction product.

[0068] Processing of the amine reaction product with the carrier is done by thoroughly mixing the amine reaction product with the carrier. Advantageously, there is no need for additional ingredients to provide a resulting substantially homogenous mixture. This mixing is done at the lowest possible temperature, i.e. just above the melting point of the carrier. The mixing step is carried out until a complete homogeneous mixture is obtained. By "homogeneous", it is meant compositions which have similar appearance to the resulting composition of a 20g of amine reaction product mixed with 80g of TAE80 for 5 minutes by means of an Ultra Turrax, the temperature of mixing being of about 70°C.

### Coating agents

[0069] When use of a carrier with a melting point between 35 and 135°C is made for the mixing with the amine reaction product, it is then preferred to further process the mixture to form a coated particle like e.g. by adsorption of the mixture onto a solid, preferably porous coating. The resulting coated particles can be in any form which is suitable for incorporation into liquid or powders, preferably powders, such as agglomerate, pellets, tablets, or mixtures thereof.

[0070] Suitable coating agents for both solid, including paste, and liquid mixture are substantially water-soluble solid binder or agglomerating agents.

[0071] "Substantially water soluble" shall refer to a material that is soluble in distilled (or equivalent) water, at 25°C., at a concentration of 0.2% by weight, and are preferably soluble at 1.0% by weight.

[0072] A "solid" is defined as a material that is a solid at ambient temperatures, and so solid substantially water-soluble binder or agglomerating agent must have a melting point of at least 30°C, and preferably of at least 40°C.

[0073] Suitable water-soluble binders or agglomerating agents include the water soluble organic polymeric compounds, water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, carbonates, bicarbonates, borates, phosphates, sulfate salts like sodium and magnesium sulfate, inorganic perhydrate salts including perborate like perborate monohydrate, percarbonate, silicates, starch, cyclodextrin, and mixtures of any of the foregoing.

[0074] Suitable organic polymeric compounds suitable as coating agents include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylcellulose and hydroxyethylcellulose, as well as carbohydrates like pectins, and gums. Further compounds are carbohydrates and derivatives such as fructose, xylose, galactose, galacturonic acid or glucose based polymers like inuline, dextran, xyloglucan, pectin or gums.

[0075] Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid



and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

**[0076]** Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

**[0077]** Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadiene pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

**[0078]** Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

**[0079]** Borate, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less than about 50°C, especially less than about 40°C.

**[0080]** Examples of carbonates are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

**[0081]** Specific examples of water-soluble phosphates are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

**[0082]** Suitable silicates include the water soluble sodium silicates with an  $\text{SiO}_2 : \text{Na}_2\text{O}$  ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.4 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an  $\text{SiO}_2 : \text{Na}_2\text{O}$  ratio of 2.0 is the most preferred silicate.

**[0083]** Typical disclosure of cyclodextrin derivatives are disclosed in WO96/05358, U.S. Pat. Nos: 3,426,011, Parmerter et al., issued Feb. 4, 1969; 3,453,257; 3,453,258; 3,453,259; and 3,453,260, all in the names of Parmerter et al., and all issued July 1, 1969; 3,459,731, Gramera et al., issued Aug. 5, 1969; 3,553,191, Parmerter et al., issued Jan. 5, 1971; 3,565,887, Parmerter et al., issued Feb. 23, 1971; 4,535,152, Szejtli et al., issued Aug. 13, 1985; 4,616,008, Hirai et al., issued Oct. 7, 1986; 4,678,598, Ogino et al., issued Jul. 7, 1987; 4,638,058, Brandt et al., issued Jan. 20, 1987; and 4,746,734, Tsuchiyama et al., issued May 24, 1988; all of said patents being incorporated herein by reference.

**[0084]** Although less preferred for use herein because of their lower solubility, partially water soluble coating agents may also be used as coating agent. These compounds are indeed less preferred because during the wash cycle the amine reaction product will still be at least partially coated and therefore can not display its full functionality of long lasting freshness on dry fabrics or hard surfaces. Examples of partially water soluble coating agents include the crystalline layered silicates. Examples of largely water insoluble builders include the sodium aluminosilicates.

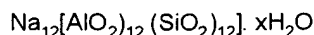
**[0085]** Crystalline layered sodium silicates have the general formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purpose of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. The most preferred material is  $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ , available from Hoechst AG as NaSKS-6.

**[0086]** Suitable aluminosilicate zeolites have the unit cell formula  $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$  wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

**[0087]** The aluminosilicate ion exchange materials can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite MAP, Zeolite HS and mixtures thereof. Zeolite A has the formula



wherein x is from 20 to 30, especially 27. Zeolite X has the formula  $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276\text{H}_2\text{O}$ .

## EP 0 971 021 A1

[0088] Typically when the amine reaction product is mixed with a carrier and further processed to form a coated particle, the amine reaction product will be present in an amount of from 1 to 75%, preferably 5 to 30%, more preferably 6 to 25% by weight of the processed reaction product in the produced particle.

[0089] Typically the coating agent will be present in an amount of from 10% to 95%, preferably from 30 to 90%, more preferably, 50 to 75% by weight of the particle of the processed amine reaction product. In this instance, the amount of carrier will be sufficient to add up to 100%. Of course, the coated particle may also contain minors but in quantities which will not exceed either of the amount of carrier material or coating agent.

[0090] Preferred coating materials are selected from carbonate, starch, cyclodextrin, and mixtures thereof.

[0091] The surface treatment of the particle can be carried out in a number of ways using equipment known in the art and the process may take in batch wise or continuous fashion.

[0092] One method for applying the coating material involves agglomeration. Any conventional agglomerator/mixer may be used including, but not limited to pan, rotary drum and vertical blender types. Molten coating compositions may also be applied either by being poured onto, or spray atomized onto a moving bed of the mixture of amine reaction product with carrier.

[0093] Another method for applying the coating is to pour the obtained mixture (so-called particle), as herein before described, onto the coating material and agglomerate it in a Braun Mixer. Care is also taken that the temperature during the mixing and/or coating step does not substantially exceed the melting point of the carrier material. For example, 150g of a mixture containing TAE80 and 20% of the amine reaction product is poured at 60°C into a Braun Mixer containing 300g of carbonate. The mixing of the ingredients is carried out for about 5 minutes. Care is also taken that the temperature during the coating does not exceed 65°C. The agglomerated particle can then be used as is for incorporation into the finished composition.

[0094] Accordingly, there is provided a processed amine reaction product as obtainable by the process of the invention.

[0095] If desired, the coated particle may also contain one or more additional ingredients like a surfactant for improved solubility or dispersability. Typical of such surfactant are the anionic, nonionic, or cationic surfactants. a cationic, anion or non-ionic surfactant like. Preferably, the weight ratio of such additional ingredient(s) to the coating agent is of up to 1:1.

[0096] In another preferred marketing execution, an additional coating on the coated particle can be provided, which depending on the nature of this additional coating will give improved storage stability, flowability and/or improved fabric substantivity of the coated particle. One typical example is polyvinyl alcohol.

### Incorporation into finished composition

[0097] The finished compositions aspect of the invention, including laundry compositions, hard surface cleaning compositions, personal cleaning compositions, comprises the incorporation of the hereinbefore described processed amine reaction product together with one or more laundry or cleaning ingredient in a finished composition.

[0098] As mentioned hereinbefore, the incorporation of the processed amine reaction product is conveniently made depending on its end form by either by spraying when in sprayable liquid form, or dry-addition when in coated form.

[0099] Laundry compositions encompass laundry detergent compositions, including liquid, solid form like powdered, tablets as well as softening compositions including rinse added softening composition as well as dryer added softening compositions.

[0100] A conventional disclosure of softening ingredients to be used in the softening composition of the invention can be found in EP 98870227.0, incorporated herein by reference.

[0101] Preferably, the finished composition is a detergent composition, more preferably in solid form.

[0102] Finished compositions incorporating the processed amine reaction product will normally contain from 0.1 to 25%, more preferably from 0.2 to 10%, and most preferably from 0.5 to 5% of the processed product on a composition weight basis.

[0103] The preferred detergent composition, embodiment of the invention, will, preferably contain a bleach precursor, a source of alkaline hydrogen peroxide necessary to form a peroxyacid bleaching species in the wash solution and preferably will also contain other components conventional in detergent compositions. Thus, preferred detergent compositions will incorporate one or more of surfactants, organic and inorganic builders, soil suspending and anti-redeposition agents, suds suppressors, enzymes, fluorescent whitening agents, photoactivated bleaches, perfumes, colours, and mixtures thereof.

[0104] Typical disclosure of such components can be found in EP-A-0,659,876 and European patent application No. 98870226.2 which are both incorporated herein by reference.

[0105] Still in another aspect of the invention, there is provided a packaged composition comprising the processed product of the invention or composition of the invention. Preferably, the packaged composition is a closed packaging system having a moisture vapour transmission rate of less than 20g/m<sup>2</sup>/24 hours. Typical disclosure of such a package can be found in WO 98/40464.

### Method of use

[0106] Also provided herein is a method for providing a delayed release of an active ketone or aldehyde which

comprises the step of contacting the surface to be treated with a compound or composition of the invention, and thereafter contacting the treated surface with a material, preferably an aqueous medium like moisture or any other means susceptible of releasing the perfume from the amine reaction product.

[0107] By "surface", it is meant any surface onto which the compound can deposit. Typical examples of such material are fabrics, hard surfaces such as dishware, floors, bathrooms, toilet, kitchen and other surfaces in need of a delayed release of a perfume ketone and/or aldehyde such as that with litter like animal litter. Preferably, the surface is selected from a fabric, a tile, a ceramic; more preferably is a fabric.

[0108] By "delayed release" is meant release of the active component (e.g perfume) over a longer period of time than by the use of the active (e.g., perfume) itself.

[0109] Still in another aspect of the invention, there is provided the use of the product of the invention for the manufacture of a laundry and cleaning composition for delivering residual fragrance and fabric care, in particular color care, onto the fabrics on which it is applied.

[0110] The following are synthesis examples of compounds as defined in the present invention:

#### I-Synthesis of ethyl 4-aminobenzoate with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde

[0111] To an ice cooled stirred solution of 10 g of 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde (0.07 mol) in 35 mL EtOH and molecular sieves (4Å, 20 g) 1eq of the amine was added via an addition funnel. The reaction mixture was stirred under nitrogen atmosphere and protected from light. After 6 days the mixture was filtrated and the solvent was removed. The yield of imine formation is about 90%.

[0112] Similar results were obtained where the 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde was replaced by bourgeonal, trans-2-nonenal, or trans-2-hexenal.

#### II-Synthesis of 1,4-bis-(3-aminopropyl)-piperazine with $\alpha$ -Damascone

[0113] In order to substitute both primary amine groups with a perfume, 2eq of perfume were used for 1eq of amino functional polymer. To an ice cooled stirred solution of 1mmol of  $\alpha$ -Damascone in 6 mL EtOH and molecular sieves (4Å, 20 g), 0.5eq of 1,4-bis-(3-aminopropyl)-piperazine was added via an addition funnel. The reaction mixture was stirred under nitrogen atmosphere and protected from light. After the disappearance of the absorption peak from the NMR spectrum of the free perfume raw material (from 3 to 16 hours), the mixture was filtrated and the solvent was removed by vacuum distillation. The yield of  $\beta$ -aminoketone formation is about 90%.

[0114] Similar results were obtained where the  $\alpha$ -Damascone was replaced by 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, vertocitral, bourgeonal,  $\delta$ -Damascone or citronellal. In these instances, Schiff-bases are formed.

#### III-Synthesis of Lupasol with Damascones and 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde

[0115] The  $\beta$ -amino ketone from Lupasol G100 (commercially available from BASF with a content of 50 % water, 50 % Lupasol G100 (Mw. 5000)) and  $\alpha$ -Damascone (or  $\delta$ -Damascone) was prepared using any one of these three different procedures described as follows:

[0116] 1. Commercially available Lupasol G100 was dried using the following procedure: 20 g of the Lupasol solution was dried at the rotating evaporator during several hours. The obtained residue, still containing about 4.5 g of H<sub>2</sub>O, was azeotropically distilled at the rotating evaporator using toluene. The residue was then placed in the desiccator dried at 60 °C (using P<sub>2</sub>O<sub>5</sub> as water absorbing material). On basis of the obtained weight we concluded that the oil contained less then 10 % H<sub>2</sub>O. On basis of the NMR-spectra we concluded that this is probably less then 5 %. This dried sample was then used in the preparation of  $\beta$ -amino ketones.

[0117] 1.38 g of the dried Lupasol G100 obtained above was dissolved in 7 ml. ethanol. The solution was stirred gently with a magnetic stirrer during a few minutes before 2 g Na<sub>2</sub> SO<sub>4</sub> (anhydrous) was added. After stirring again for a few minutes 2.21 g  $\alpha$ -Damascone was added over a period of 1 minute. After two days reaction, the mixture was filtrated over a Celite filter (vide supra), and the residue washed thoroughly with ethanol. About 180 ml. of a light foaming filtrate was obtained. This was concentrated until dryness using a rotating evaporator and dried over P<sub>2</sub>O<sub>5</sub> in an desiccator at room temperature. About 3.5 of a colorless oil was obtained.

[0118] 2. 4.3 g Lupasol G100 solution was without drying dissolved in 10 ml. ethanol. The solution was stirred with a magnetic stirrer during a few minutes before 3.47 g  $\alpha$ -Damascone was added over a 1.5 minutes period. After two days reaction at room temperature the reaction mixture was filtrated over Celite (vide supra) and the residue washed thoroughly with ethanol. The filtrate (200 ml., light foaming) was concentrated at the evaporator and dried in an desiccator (P<sub>2</sub>O<sub>5</sub> as drying agent) at room temperature. About 5.9 g of a colorless oil was obtained.

[0119] 3. To 3.0 g of Lupasol G100 solution (used as such) was added 2.41 g  $\alpha$ -Damascone. The mixture was stirred without using solvent. After stirring for 4 days the obtained oil was dissolved in 100 ml. THF, dried with MgSO<sub>4</sub>, filtrated and the filtrate concentrated at the rotating evaporator. After drying in the desiccator (P<sub>2</sub>O<sub>5</sub>) at room temperature about 4 g of a colorless oil was obtained. This oil still contained about 13 % (w/w) of THF, even after a prolonged drying (3 days).

[0120] The product obtained from the three procedures had identical NMR-spectra.

[0121] Similar results are obtained where Lupasol G35 or Lupasol HF is used instead of Lupasol G100.

[0122] Similar results were obtained where the  $\alpha$ -Damascone was replaced by 2,4-dimethyl-3-cyclohexen-1-

carboxaldehyde.

**[0123]** Still another possible route of synthesis is by using Lupasol P. The  $\beta$ -amino ketone from Lupasol P and  $\alpha$ -Damascone was prepared using the procedure described as follows:

**[0124]** 1.8g Lupasol P solution (50 % H<sub>2</sub>O, 50 % Lupasol Mw. 750000, as obtained from BASF) was dissolved in 7 ml ethanol, the solution was stirred for a few minutes with a magnetic stirrer before 1.44 g  $\alpha$ -Damascone was added. After three days the reaction mixture was filtrated over a celite filter (vide supra) and the residue washed thoroughly with ethanol. After concentrating of the filtrate and drying of the obtained oil in the desiccator (P<sub>2</sub>O<sub>5</sub>) at room temperature, about 3 g of the reaction product between Lupasol and  $\alpha$ -Damascone was obtained.

### Processing method

**[0125]** Processing of the amine reaction product with the carrier is done as hereinbefore described. In particular, 20g of amine reaction product as above synthesised is mixed in an Ultra Turrax containing 80g of carrier, e.g. TAE80 for 5 minutes, the temperature of mixing being of about 70°C, and the speed of the mixer being sufficient so as to maintain such temperature substantially constant. Temperature and time will depend on the nature of the carrier but are a conventional step to skilled man. The resulting mixture is maintained at a temperature substantially equal to the melting point of the carrier material. Once the mixture is at a suitable temperature, it is poured onto the coating material and agglomerated in an electrical mixer like a Braun Mixer. Care is also taken that the temperature during the mixing does not substantially exceed the melting point of the carrier material. For example, 150g of a mixture containing TAE80 and 20% of the amine reaction product is poured at 60°C into a Braun Mixer containing 300g of carbonate. The mixing of the ingredients is carried out for about 5 minutes. Care is also taken that the temperature during the mixing does not exceed 65°C. Again, temperature and time will depend on the nature of the coating agent but are conventional step to skilled man.

### Abbreviations used in the following laundry and cleaning composition Examples

**[0126]** In the laundry and cleaning compositions, the abbreviated component identifications have the following meanings:

DEQA	Di-(tallowyl-oxy-ethyl) dimethyl ammonium chloride
DTDMAC	Ditallow dimethylammonium chloride
DEQA (2)	Di-(soft-tallowyloxyethyl) hydroxyethyl methyl ammonium methylsulfate.
DTDMAMS	Ditallow dimethyl ammonium methylsulfate.
SDASA	1:2 ratio of stearyl dimethyl amine:triple-pressed stearic acid.
Fatty acid	Stearic acid of IV=0
Electrolyte	Calcium chloride
PEG	Polyethylene Glycol 4000
Neodol 45-13	C14-C15 linear primary alcohol ethoxylate, sold by Shell Chemical CO.
Silicone antifoam	Polydimethylsiloxane foam controller with siloxaneoxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
PEI	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
HEDP	1,1 -hydroxyethane diphosphonic acid
LAS	Sodium linear C <sub>11-13</sub> alkyl benzene sulfonate
TAS	Sodium tallow alkyl sulfate
CxyAS	Sodium C <sub>1x</sub> -C <sub>1y</sub> alkyl sulfate
C46SAS	Sodium C <sub>14</sub> -C <sub>16</sub> secondary (2,3) alkyl sulfate
CxyEzS	Sodium C <sub>1x</sub> -C <sub>1y</sub> alkyl sulfate condensed with z moles of ethylene oxide
CxyEz	C <sub>1x</sub> -C <sub>1y</sub> predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
QAS	R <sub>2</sub> -N <sup>+</sup> <sub>a</sub> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>12</sub> - C <sub>14</sub>
QAS 1	R <sub>2</sub> -N <sup>+</sup> <sub>a</sub> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>8</sub> - C <sub>11</sub>
APA	C <sub>8</sub> - C <sub>10</sub> amido propyl dimethyl amine
Soap	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
STS	Sodium toluene sulphonate
CFAA	C <sub>12</sub> -C <sub>14</sub> (coco) alkyl N-methyl glucamide

EP 0 971 021 A1

	TFAA	C <sub>16</sub> -C <sub>18</sub> alkyl N-methyl glucamide
	TPKFA	C <sub>12</sub> -C <sub>14</sub> topped whole cut fatty acids
	STPP	Anhydrous sodium tripolyphosphate
	TSPP	Tetrasodium pyrophosphate
5	Zeolite A	Hydrated sodium aluminosilicate of formula Na <sub>12</sub> (AlO <sub>2</sub> SiO <sub>2</sub> ) <sub>12</sub> ·27H <sub>2</sub> O having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
	NaSKS-6	Crystalline layered silicate of formula δ- Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>
	Citric acid	Anhydrous citric acid
10	Borate	Sodium borate
	Carbonate	Anhydrous sodium carbonate with a particle size between 200µm and 900µm
	Bicarbonate	Anhydrous sodium bicarbonate with a particle size distribution between 400µm and 1200µm
	Silicate	Amorphous sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O = 2.0:1)
15	Sulfate	Anhydrous sodium sulfate
	Mg sulfate	Anhydrous magnesium sulfate
	Citrate	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850µm
20	MA/AA	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
	MA/AA (1)	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000
	AA	Sodium polyacrylate polymer of average molecular weight 4,500
	CMC	Sodium carboxymethyl cellulose
	Cellulose ether	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
25	Protease	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase
	Protease I	Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
30	Alcalase	Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
	Cellulase	Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
	Amylase	Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
35	Lipase	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase
	Lipase (1)	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
	Endolase	Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
40	PB4	Sodium perborate tetrahydrate of nominal formula NaBO <sub>2</sub> ·3H <sub>2</sub> O·H <sub>2</sub> O <sub>2</sub>
	PB1	Anhydrous sodium perborate bleach of nominal formula NaBO <sub>2</sub> ·H <sub>2</sub> O <sub>2</sub>
	Percarbonate	Sodium percarbonate of nominal formula 2Na <sub>2</sub> CO <sub>3</sub> ·3H <sub>2</sub> O <sub>2</sub>
	NOBS	Nonanoyloxybenzene sulfonate in the form of the sodium salt
45	NAC-OBS	(6-nonamidocaproyl) oxybenzene sulfonate
	TAED	Tetraacetythylenediamine
	DTPA	Diethylene triamine pentaacetic acid
	DTPMP	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
50	EDDS	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
	Photoactivated bleach (1)	Sulfonated zinc phthlocyanine encapsulated in dextrin soluble polymer
	Photoactivated bleach (2)	Sulfonated aluminophthlocyanine encapsulated in dextrin soluble polymer
55	Brightener 1	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
	Brightener 2	Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino stilbene-2,2'-disulfonate

EP 0 971 021 A1

	HEDP	1,1 -hydroxyethane diphosphonic acid
	PEGx	Polyethylene glycol, with a molecular weight of x (typically 4,000)
	PEO	Polyethylene oxide, with an average molecular weight of 50,000
	TEPAE	Tetraethylenepentaamine ethoxylate
5	PVI	Polyvinyl imidosole, with an average molecular weight of 20,000
	PVP	Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000
	PVNO	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
	PVPVI	Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
10	QEA	bis((C <sub>2</sub> H <sub>5</sub> O)(C <sub>2</sub> H <sub>4</sub> O) <sub>n</sub> )(CH <sub>3</sub> ) -N <sup>+</sup> <sub>a</sub> -C <sub>6</sub> H <sub>12</sub> -N <sup>+</sup> <sub>a</sub> -(CH <sub>3</sub> ) bis((C <sub>2</sub> H <sub>5</sub> O)-(C <sub>2</sub> H <sub>4</sub> O)) <sub>n</sub> , wherein n = from 20 to 30
	SRP 1	Anionically end capped poly esters
	SRP 2	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
15	PEI	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
	Silicone antifoam	Polydimethylsiloxane foam controller with siloxaneoxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
	Opacifier	Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
20	Wax	Paraffin wax
	PA30	Polyacrylic acid of average molecular weight of between about 4,500 - 8,000.
	480N	Random copolymer of 7:3 acrylate/methacrylate, average molecular weight about 3,500.
	Polygel/carbopol	High molecular weight crosslinked polyacrylates.
25	Metasilicate	Sodium metasilicate (SiO <sub>2</sub> :Na <sub>2</sub> O ratio = 1.0).
	Nonionic	C <sub>13</sub> -C <sub>15</sub> mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5.
	Neodol 45-13	C14-C15 linear primary alcohol ethoxylate, sold by Shell Chemical CO.
30	MnTACN	Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane.
	PAAC	Pentaamine acetate cobalt(III) salt.
	Paraffin	Paraffin oil sold under the tradename Winog 70 by Wintershall.
	NaBz	Sodium benzoate.
	BzP	Benzoyl Peroxide.
35	SCS	Sodium cumene sulphonate.
	BTA	Benzotriazole.
	PH	Measured as a 1% solution in distilled water at 20°C.
	PARP1	Processed amine reaction product of ethyl 4-aminobenzoate with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde as made from Synthesis example I, mixed with a carrier and agglomerated with TAE80 coating agent according to processing method above described.
40	PARP2	Processed amine reaction product of Lupasol G35 with α-Damascone as made from Synthesis example III, mixed with a carrier and agglomerated with TAE100 coating agent according to processing method above described.
	PARP3	Processed amine reaction product of Lupasol HF with 6-Damascone as made from Synthesis example III, mixed with a carrier and agglomerated with TAE80 coating agent according to processing method above described.
45	PARP4	Processed amine reaction product of BNPP with 6-Damascone as made from Synthesis example II, mixed with a carrier and agglomerated with PEG4000 coating agent according to processing method above described.
	PARP5	Processed amine reaction product of LupasolG100 with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde as made from Synthesis example III, mixed with a carrier and agglomerated with TAE80 coating agent according to processing method above described.
50	PARP6	Processed amine reaction product of ethyl 4-aminobenzoate with trans-2-nonenal as made from Synthesis example I, mixed with a carrier and agglomerated with TAE80 coating agent according to processing method above described.
55	PARP7	Processed amine reaction product of ethyl 4-aminobenzoate with trans-2-hexenal as made from Synthesis example I, mixed with a carrier and agglomerated with TAE80 coating agent according to processing method above described.

[0127] In the following formulation examples all levels are quoted as % by weight of the composition unless otherwise stated, and incorporation of the processed amine reaction product so called herein after "PARP" in the fully formulated composition is carried out by dry addition (d) in the composition as defined herein before. The term in bracket for the PARP in the formulation examples refers to the type of carrier (c) for carbonate carrier and (s) for starch carrier.

#### Example 1

[0128] The following high density granular laundry detergent compositions A to F were prepared in accord with the invention:

	A0	A1	A	B	C	D	E	F
LAS	6.0	6.0	8.0	8.0	8.0	2.0	6.0	6.0
TAS	1.0	0.1	-	0.5	-	0.5	1.0	0.1
C46(S)AS	-	-	2.0	2.5	-	-	-	-
C25AS	4.5	5.5	-	-	-	7.0	4.5	5.5
C68AS	-	-	2.0	5.0	7.0	-	-	-
C25E5	4.6	4.6	-	-	3.4	10.0	4.6	4.6
C25E7	-	-	3.4	3.4	1.0	-	-	-
C25E3S	5.0	4.5	-	-	-	2.0	5.0	4.5
QAS	-	-	-	0.8	-	-	-	-
QAS (I)	0.5	1.0	-	-	-	0.8	0.5	1.0
Zeolite A	20.0	18.1	18.1	18.0	14.1	18.1	20.0	18.1
Citric acid	-	2.5	-	-	-	2.5	-	2.5
Carbonate	10.0	13.0	13.0	13.0	25.0	10.0	10.0	13.0
SKS-6	-	10.0	-	-	-	10.0	-	10.0
Silicate	0.5	0.3	1.4	1.4	3.0	0.3	0.5	0.3
Citrate	-	-	-	1.0	-	3.0	-	-
Sulfate	-	-	26.1	26.1	26.1	6.0	-	-
Mg sulfate	-	0.2	0.3	-	-	0.2	-	0.2
MA/AA	1.0	1.0	0.3	0.3	0.3	4.0	1.0	1.0
CMC	0.4	0.4	0.2	0.2	0.2	0.2	0.4	0.4
PB4	-	-	9.0	9.0	5.0	-	-	-
Percarbonate	18.0	18.0	-	-	-	-	18.0	18.0
TAED	3.9	4.2	1.5	0.4	1.5	-	3.9	4.2
NAC-OBS	-	-	-	2.0	1.0	-	-	-
DTPMP	-	-	0.25	0.25	0.25	0.25	-	-
SRP2	-	0.2	-	-	-	0.2	-	0.2
EDDS	0.5	0.5	-	0.25	0.4	-	0.5	0.5
CFAA	-	-	-	1.0	-	2.0	-	-
HEDP	0.4	0.4	0.3	0.3	0.3	0.3	0.4	0.4
QEA	-	0.5	-	-	-	0.2	-	0.5
Protease I	-	-	-	-	0.26	1.0	-	-
Protease	1.5	1.0	0.26	0.26	-	-	1.5	1.0
Cellulase	0.3	0.3	0.3	-	-	0.3	0.3	0.3
Amylase	0.5	0.5	0.1	0.1	0.1	0.4	0.5	0.5
Lipase (1)	0.5	0.5	0.3	-	-	0.5	0.5	0.5
Photoactivated bleach (ppm)	20 ppm	20 ppm	15 ppm	15 ppm	15 ppm	-	20 ppm	20 ppm
PVNO/PVPVI	-	-	-	-	-	0.1	-	-
Brightener 1	0.09	0.09	0.09	0.09	0.09	-	0.09	0.09
Perfume spray on	0.4	0.4	0.3	0.3	0.3	0.4	0.4	0.4
PARP 3	-	-	10 (c)	5 (s)	-	-	5(c)	1 (c)

**EP 0 971 021 A1**

	A0	A1	A	B	C	D	E	F
PARP 5	-	-	-	-	2 (c)	8 (c)	4 (s)	-
PARP 6	5(c)	1 (c)	-	-	-	-	-	-
PARP 7	4 (s)	-	-	-	-	-	-	-
Silicone antifoam	0.3	0.3	0.5	0.5	0.5	-	0.3	0.3
Misc/minors to 100%								
Density in g/litre	850	850	850	850	850	850	850	850

**Example 2**

**[0129]** The following granular laundry detergent compositions G to L of particular utility under European machine wash conditions were prepared in accord with the invention:

	G	H	I	J	K	L
LAS	5.5	7.5	5.0	5.0	6.0	7.0
TAS	1.25	1.86	-	0.8	0.4	0.3
C24AS/C25AS	-	2.24	5.0	5.0	5.0	2.2
C25E3S	-	0.76	1.0	1.5	3.0	1.0
C45E7	3.25	-	-	-	-	3.0
TFAA	-	-	2.0	-	-	-
C25E5	-	5.5	-	-	-	-
QAS	0.8	-	-	-	-	-
QAS II	-	0.7	1.0	0.5	1.0	0.7
STPP	19.7	-	-	-	-	-
Zeolite A	-	19.5	25.0	19.5	20.0	17.0
NaSKS-6/citric acid (79:21)	-	10.6	-	10.6	-	-
NaSKS-6	-	-	9.0	-	10.0	10.0
Carbonate	6.1	10.0	9.0	10.0	10.0	18.0
Bicarbonate	-	2.0	7.0	5.0	-	2.0
Silicate	6.8	-	-	0.3	0.5	-
Citrate	-	-	4.0	4.0	-	-
Sulfate	39.8	-	-	5.0	-	12.0
Mg sulfate	-	-	0.1	0.2	0.2	-
MA/AA	0.5	1.6	3.0	4.0	1.0	1.0
CMC	0.2	0.4	1.0	1.0	0.4	0.4
PB4	5.0	12.7	-	-	-	-
Percarbonate	-	-	-	-	18.0	15.0
TAED	0.5	3.1	-	-	5.0	-
NAC-OBS	1.0	3.5	-	-	-	2.5
DTPMP	0.25	0.2	0.3	0.4	-	0.2
HEDP	-	0.3	-	0.3	0.3	0.3
QEA	-	-	1.0	1.0	1.0	-
Protease I	-	-	-	0.5	1.2	-
Protease	0.26	0.85	0.9	1.0	-	0.7
Lipase (1)	0.15	0.15	0.3	0.3	0.3	0.2
Cellulase	0.28	0.28	0.2	0.2	0.3	0.3
Amylase	0.1	0.1	0.4	0.4	0.6	0.2
PVNO/PVPVI	-	-	0.2	0.2	-	-
PVP	0.9	1.3	-	-	-	0.9
SRP 1	-	-	0.2	0.2	0.2	-



**EP 0 971 021 A1**

	<b>G</b>	<b>H</b>	<b>I</b>	<b>J</b>	<b>K</b>	<b>L</b>
Photoactivated bleach (1) (ppm)	15 ppm	27 ppm	-	-	20 ppm	20 ppm
Photoactivated bleach (2) (ppm)	15 ppm	-	-	-	-	-
Brightener 1	0.08	0.19	-	-	0.09	0.15
Brightener 2	-	0.04	-	-	-	-
Perfume	0.3	0.3	0.4	0.3	0.4	0.3
PARP1	1.0 (c)	10.0(c)	5.0 (c)	-	-	-
PARP2	-	-	2.0 (c)	4.0 (s)	8.0 (c)	2.0 (c)
Silicone antifoam	0.5	2.4	0.3	0.5	0.3	2.0
Minors/misc to 100%						
Density in g/litre	750	750	750	750	750	750

**Example 3**

**[0130]** The following detergent formulations of particular utility under European machine wash conditions were prepared in accord with the invention.

	<b>M</b>	<b>N</b>	<b>O</b>	<b>P</b>
Blown powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	24.0	-	-	20.0
STPP	-	27.0	24.0	-
Sulfate	4.0	6.0	13.0	-
MA/AA	1.0	4.0	6.0	2.0
Silicate	1.0	7.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
Brightener 1	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DTPMP	0.4	0.4	0.2	0.4
Spray on				
Brightener	0.02	-	-	0.02
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.5	0.3	0.5	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
QEA	-	-	-	1.0
EDDS	0.3	-	-	-
Sulfate	2.0	3.0	5.0	10.0
Carbonate	6.0	13.0	11.0	14.0
Citric acid	2.5	-	-	2.0
QAS II	0.5	-	-	0.5
SKS-6	10.0	-	-	-
Percarbonate	18.5	-	-	-
PB4	-	18.0	10.0	21.5
TAED	2.0	2.0	-	2.0
NAC-OBS	3.0	2.0	4.0	-
Protease	1.0	1.0	1.0	1.0

**EP 0 971 021 A1**

	M	N	O	P
Dry additives				
Lipase	-	0.4	-	0.2
Lipase (1)	0.4	-	0.4	-
Amylase	0.2	0.2	0.2	0.4
Brightener 1	0.05	-	-	0.05
PARP3	2.0 (c)	1.0 (c)	4.0 (s)	2.0 (c)
Misc/minor to 100%				

**Example 4**

**[0131]** The following granular detergent formulations were prepared in accord with the invention.

	Q	R	S	T	U	V
Blown powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-
C45AES	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
Zeolite A	10.0	18.0	14.0	12.0	10.0	10.0
MA/AA	-	0.5	-	-	-	2.0
MA/AA (1)	7.0	-	-	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sulfate	5.0	6.3	14.3	11.0	15.0	19.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0
Carbonate	13.0	19.0	8.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
DTPA	-	0.9	0.5	-	-	0.5
Brightener 2	0.3	0.2	0.3	-	0.1	0.3
Spray on						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
LAS	-	2.0	2.0	-	-	2.0
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5
Misc (water etc)	-	2.0	2.0	2.0	-	2.0
Dry additives						
QAS (I)	-	-	-	-	1.0	-
Citric acid	-	-	-	-	2.0	-
PB4	-	-	-	-	12.0	1.0
PB1	4.0	1.0	3.0	2.0	-	-
Percarbonate	-	-	-	-	2.0	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	0.6

**EP 0 971 021 A1**

	Q	R	S	T	U	V
Dry additives						
Methyl cellulose	0.2	-	-	-	-	-
SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Cumene sulfonic acid	-	1.0	-	-	-	2.0
Lipase	0.2	-	0.2	-	0.2	0.4
Cellulase	0.2	0.2	0.2	0.3	0.2	0.2
Amylase	0.2	-	0.1	-	0.2	-
Protease	0.5	0.5	0.5	0.3	0.5	0.5
PVPVI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP1	0.2	0.5	0.3	-	0.2	-
PARP3	2.0(c)	1.0(c)	4.0(c)	0.5(c)	3.5(c)	1.0(s)
Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	-	-	0.2	-	0.2	-
Misc/minors to 100%						

**Example 5**

**[0132]** The following nil bleach-containing detergent formulations of particular use in the washing of coloured clothing, according to the present invention were prepared:

	W	X	Y
Blown Powder			
Zeolite A	15.0	15.0	-
Sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0

**EP 0.971 021 A1**

	W	X	Y
Dry additives			
Bicarbonate	7.0	3.0	5.0
Carbonate	6.0	-	7.0
PVPVI/PVNO	0.5	0.5	0.5
Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
PARP1	7.0(c)	10(c)	5.0(c)
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sulfate	0.0	9.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	700	700	700

**Example 6**

**[0133]** The following granular detergent formulations were prepared in accord with the invention.

	Z	AA	BB	CC
Base granule				
Zeolite A	30.0	22.0	24.0	10.0
Sulfate	10.0	5.0	10.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA (1)	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0
C45AES	-	1.0	1.0	-
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	10.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray on				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
Dry additives				
Carbonate	5.0	5.0	15.0	6.0
PVPVI/PVNO	0.5	-	0.3	-
Protease	1.0	1.0	1.0	0.5
Lipase	0.4	-	-	0.4
Amylase	0.1	-	-	0.1
Cellulase	0.1	0.2	0.2	0.1
NOBS	-	4.0	-	4.5
PB1	1.0	5.0	1.5	6.0

**EP 0 971 021 A1**

	<b>Z</b>	<b>AA</b>	<b>BB</b>	<b>CC</b>
Dry additives				
Sulfate	4.0	5.0	-	5.0
SRPI	-	0.4	-	-
PARP1	10(c)	5.0(c)	8.0(c)	-
PARP3	-	1.0(s)	-	2.0(s)
Sud supressor	-	0.5	0.5	-
Misc/minor to 100%				

Example 7

**[0134]** The following granular detergent compositions were prepared in accord with the invention.

	<b>DD</b>	<b>EE</b>	<b>FF</b>
Blown powder			
Zeolite A	20.0	-	15.0
STPP	-	20.0	-
Sulphate	-	-	5.0
Carbonate	-	-	5.0
TAS	-	-	1.0
LAS	6.0	6.0	6.0
C68AS	2.0	2.0	-
Silicate	3.0	8.0	-
MA/AA	4.0	2.0	2.0
CMC	0.6	0.6	0.2
Brightener 1	0.2	0.2	0.1
DTPMP	0.4	0.4	0.1
STS	-	-	1.0
Spray on			
C45E7	5.0	5.0	4.0
Silicone antifoam	0.3	0.3	0.1
Perfume	0.2	0.2	0.3
Dry additives			
QEA	-	-	1.0
Carbonate	14.0	9.0	10.0
PB1	1.5	2.0	-
PB4	18.5	13.0	13.0
TAED	2.0	2.0	2.0
QAS(I)	-	-	1.0
Photoactivated bleach	15 ppm	15 ppm	15ppm
SKS-6	-	-	3.0
Protease	1.0	1.0	0.2
Lipase	0.2	0.2	0.2
Amylase	0.4	0.4	0.2
Cellulase	0.1	0.1	0.2
Sulfate	10.0	20.0	5.0
PARP3	5.0(c)	2.0(c)	4.0(s)
Misc/minors to 100%			
Density (g/litre)	700	700	700

# EP 0 971 021 A1

## Example 8

[0135] The following detergent compositions, according to the present invention were prepared:

	GG	HH	II
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.2	0.4
EDDS	-	0.4	0.2
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
PEO	-	-	0.2
PARP3	2.0(c)	1.0(c)	0.75(c)
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	850	850	850

## Example 9

[0136] The following detergent formulations, according to the present invention were prepared:

	JJ	KK	LL	MM
LAS	18.0	14.0	24.0	20.0

EP 0 971 021 A1

	JJ	KK	LL	MM
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C23E56.5	-	-	1.0	-
C45E7	-	1.0	-	-
C45E3S	1.0	2.5	1.0	-
STPP	32.0	18.0	30.0	22.0
Silicate	9.0	5.0	9.0	8.0
Carbonate	9.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
PB1	3.0	1.0	-	-
PB4	-	1.0	-	-
NOBS	2.0	1.0	-	-
DTPMP	-	1.0	-	-
DTPA	0.5	-	0.2	0.3
SRP 1	0.3	0.2	-	0.1
MA/AA	1.0	1.5	2.0	0.5
CMC	0.8	0.4	0.4	0.2
PEI	-	-	0.4	-
Sodium sulfate	20.0	10.0	20.0	30.0
Mg sulfate	0.2	-	0.4	0.9
Protease	0.8	1.0	0.5	0.5
Amylase	0.5	0.4	-	0.25
Lipase	0.2	-	0.1	-
Cellulase	0.15	-	-	0.05
Photoactivated bleach (ppm)	30ppm	20ppm	-	10ppm
PARP4	2.0(c)	4.0(s)	8.0(c)	0.8(c)
Perfume spray on	0.3	0.3	0.1	0.2
Brightener 1/2	0.05	0.2	0.08	0.1
Misc/minors to 100%				

Example 10

[0137] The following liquid detergent formulations were prepared in accord with the invention (levels are given as parts per weight).

	NN	OO	PP	QQ	RR
LAS	11.5	8.8	-	3.9	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	15.7	-
C23E9	-	2.7	1.8	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.2	-	3.1
TPKFA	1.6	-	2.0	0.5	2.0
Citric acid (50%)	6.5	1.2	2.5	4.4	2.5
Calcium formate	0.1	0.06	0.1	-	-
Sodium formate	0.5	0.06	0.1	0.05	0.05
Sodium cumene sulfonate	4.0	1.0	3.0	1.18	-
Borate	0.6	-	3.0	2.0	2.9
Sodium hydroxide	5.8	2.0	3.5	3.7	2.7

**EP 0 971 021 A1**

	<b>NN</b>	<b>OO</b>	<b>PP</b>	<b>QQ</b>	<b>RR</b>
Ethanol	1.75	1.0	3.6	4.2	2.9
1, 2 propanediol	3.3	2.0	8.0	7.9	5.3
Monoethanolamine	3.0	1.5	1.3	2.5	0.8
TEPAE	1.6	-	1.3	1.2	1.2
Protease	1.0	0.3	1.0	0.5	0.7
Lipase	-	-	0.1	-	-
Cellulase	-	-	0.1	0.2	0.05
Amylase	-	-	-	0.1	-
SRP1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
PARP1	8.0(c)	-	-	-	-
PARP2	-	2.0(c)	-	-	-
PARP3	-	-	1.0(c)	-	-
PARP4	-	-	-	4.0(s)	-
PARP5	-	-	-	-	10.0(s)
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Water/minors up to 100%					

**Example 11**

**[0138]** The following liquid detergent formulations were prepared in accord with the invention (levels are given in Darts per weight):

	<b>SS</b>	<b>TT</b>	<b>UU</b>	<b>VV</b>	<b>WW</b>	<b>XX</b>	<b>YY</b>	<b>ZZ</b>
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
APA	-	1.4	-	-	3.0	1.0	2.0	-
TPKFA	2.0	-	13.0	7.0	-	15.0	11.0	11.0
Citric acid	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl/tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Rape seed fatty acid	4.0	2.0	1.0	-	1.0	-	3.5	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	-	5.0	-	-	9.0	9.0
Triethanolamine	-	-	8.0	-	-	-	-	-
TEPAE	0.5	-	0.5	0.2	-	-	0.4	0.3
DTPMP	1.0	1.0	0.5	1.0	2.0	1.2	1.0	-
Protease	0.5	0.5	0.4	0.25	-	0.5	0.3	0.6
Alcalase	-	-	-	-	1.5	-	-	-
Lipase	-	0.10	-	0.01	-	-	0.15	0.15
Amylase	0.25	0.25	0.6	0.5	0.25	0.9	0.6	0.6
Cellulase	-	-	-	0.05	-	-	0.15	0.15
Endolase	-	-	-	0.10	-	-	0.07	-
SRP2	0.3	-	0.3	0.1	-	-	0.2	0.1



**EP 0 971 021 A1**

	SS	TT	UU	VV	WW	XX	YY	ZZ
Boric acid	0.1	0.2	1.0	2.0	1.0	1.5	2.5	2.5
Calcium chloride	-	0.02	-	0.01	-	-	-	-
Bentonite clay	-	-	-	-	4.0	4.0	-	-
Brightener 1	-	0.4	-	-	0.1	0.2	0.3	-
Sud supressor	0.1	0.3	-	0.1	0.4	-	-	-
Opacifier	0.5	0.4	-	0.3	0.8	0.7	-	-
PARP1	8(s)	-	5(c)	-	3(c)	-	4(s)	2(s)
PARP3	-	2(c)	-	1(c)	-	8(c)	1(c)	0.7(c)
Water/minors up to 100%								
NaOH up to pH	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2

**Example 12**

**[0139]** The following liquid detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

	AB	AC
LAS	27.6	18.9
C45AS	13.8	5.9
C13E8	3.0	3.1
Oleic acid	3.4	2.5
Citric acid	5.4	5.4
Sodium hydroxide	0.4	3.6
Calcium formate	0.2	0.1
Sodium formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	5.9	5.5
Xylene sulfonic acid	-	2.4
TEPAE	1.5	0.8
Protease	1.5	0.6
PEG	-	0.7
Brightener 2	0.4	0.1
Perfume spray on	0.5	0.3
PARP2	2.0(c)	-
PARP4	2.0(c)	1.0(c)
Water/minors up to 100%		

**Example 13**

**[0140]** The following laundry bar detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

	AD	AE	AF	AG	AH	AI	AJ	AK
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Sodium laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25

**EP 0 971 021 A1**

	AD	AE	AF	AG	AH	AI	AJ	AK
Carbonate	10.0	-	11.0	5.0	2.0	7.0	13.0	9.0
Calcium carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DTPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Protease	-	0.12	-	0.08	0.08	-	-	0.1
Lipase	-	0.1	-	0.1	-	-	-	-
Amylase	-	-	0.8	-	-	-	0.1	-
Cellulase	-	0.15	-	-	0.15	0.1	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
PARP1	10(c)	-	-	-	-	8(c)	-	-
PARP2	-	4(c)	-	-	-	-	2(c)	-
PARP3	-	-	2(c)	-	-	-	-	1(c)
PARP4	-	-	-	4(s)	-	-	-	-
PARP5	-	-	-	-	10(c)	-	-	4(c)
Brightener	0.15	0.10	0.15	-	-	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

**Example 14**

**[0141]** The following detergent additive compositions were prepared according to the present invention :

	AL	AM	AN
LAS	-	5.0	5.0
STPP	30.0	-	20.0
Zeolite A	-	35.0	20.0
PB1	20.0	15.0	-
TAED	10.0	8.0	-
PARP1	10.0(c)	-	5.0(c)
PARP3	-	4.0(c)	2.0(c)
Protease	-	0.3	0.3
Amylase	-	0.06	0.06
Minors, water and miscellaneous	Up to 100%		

**Example 15**

**[0142]** The following compact high density (0.96Kg/l) dishwashing detergent compositions were prepared

**EP 0 971 021 A1**

according to the present invention :

	AO	AP	AQ	AR	AS	AT	AU	AV
STPP	-	-	54.3	51.4	51.4	-	-	50.9
Citrate	35.0	17.0	-	-	-	46.1	40.2	-
Carbonate	-	15.0	12.0	14.0	4.0	-	7.0	31.1
Bicarbonate	-	-	-	-	-	25.4	-	-
Silicate	32.0	14.8	14.8	10.0	10.0	1.0	25.0	3.1
Metasilicate	-	2.5	-	9.0	9.0	-	-	-
PB1	1.9	9.7	7.8	7.8	7.8	-	-	-
PB4	8.6	-	-	-	-	-	-	-
Percarbonate	-	-	-	-	-	6.7	11.8	4.8
Nonionic	1.5	2.0	1.5	1.7	1.5	2.6	1.9	5.3
TAED	5.2	2.4	-	-	-	2.2	-	1.4
HEDP	-	1.0	-	-	-	-	-	-
DTPMP	-	0.6	-	-	-	-	-	-
MnTACN	-	-	-	-	-	-	0.008	-
PAAC	-	-	0.008	0.01	0.007	-	-	-
BzP	-	-	-	-	1.4	-	-	-
Paraffin	0.5	0.5	0.5	0.5	0.5	0.6	-	-
PARP3	2(c)	4(c)	2(c)	1(c)	-	-	-	0.5(c)
PARP1	-	-	-	-	10(c)	3(s)	2(c)	-
Protease	0.072	0.072	0.029	0.053	0.046	0.026	0.059	0.06
Amylase	0.012	0.012	0.006	0.012	0.013	0.009	0.017	0.03
Lipase	-	0.001	-	0.005	-	-	-	-
BTA	0.3	0.3	0.3	0.3	0.3	-	0.3	0.3
MA/AA	-	-	-	-	-	-	4.2	-
480N	3.3	6.0	-	-	-	-	-	0.9
Perfume	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1
Sulphate	7.0	20.0	5.0	2.2	0.8	12.0	4.6	-
pH	10.8	11.0	10.8	11.3	11.3	9.6	10.8	10.9
Miscellaneous and water	Up to 100%							

**Example 16**

**[0143]** The following granular dishwashing detergent compositions of bulk density 1.02Kg/L were prepared according to the present invention :

	AW	AX	AY	AZ	BA	BC	BD	BE
STPP	30.0	30.0	33.0	34.2	29.6	31.1	26.6	17.6
Carbonate	29.5	30.0	29.0	24.0	15.0	36.0	2.1	38.0
Silicate	7.4	7.4	7.5	7.2	13.3	3.4	43.7	12.4
Metasilicate	-	-	4.5	5.1	-	-	-	-
Percarbonate	-	-	-	-	-	4.0	-	-
PB1	4.4	4.2	4.5	4.5	-	-	-	-
NADCC	-	-	-	-	2.0	-	1.6	1.0
Nonionic	1.2	1.0	0.7	0.8	1.9	0.7	0.6	0.3
TAED	1.0	-	-	-	-	0.8	-	-
PAAC	-	0.004	0.004	0.004	-	-	-	-
BzP	-	-	-	1.4	-	-	-	-
Paraffin	0.25	0.25	0.25	0.25	-	-	-	-

**EP 0 971 021 A1**

	AW	AX	AY	AZ	BA	BC	BD	BE
PARP3	1.0(c)	0.5(c)	4.0(s)	8.0(c)	-	-	1.0(c)	0.5(c)
PARP1	-	-	-	-	10(c)	5.0(c)	2.0(c)	8.0(s)
Protease	0.036	0.015	0.03	0.028	-	0.03	-	-
Amylase	0.003	0.003	0.01	0.006	-	0.01	-	-
Lipase	0.005	-	0.001	-	-	-	-	-
BTA	0.15	0.15	0.15	0.15	-	-	-	-
Perfume	0.2	0.2	0.2	0.2	0.1	0.2	0.2	-
Sulphate	23.4	25.0	22.0	18.5	30.1	19.3	23.1	23.6
pH	10.8	10.8	11.3	11.3	10.7	11.5	12.7	10.9
Miscellaneous and water	Up to 100%							

Example 17

**[0144]** The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm<sup>2</sup> using a standard 12 head rotary press:

	BF	BJ	BK	BL	BM	BN
STPP	-	48.8	49.2	38.0	-	46.8
Citrate	26.4	-	-	-	31.1	-
Carbonate	-	4.0	12.0	14.4	10.0	20.0
Silicate	26.4	14.8	15.0	12.6	17.7	2.4
PARP1	3.0(c)	-	-	-	5.0(c)	-
PARP2	-	2.0(c)	-	-	-	4.0(c)
PARP3	-	-	2.0(c)	1(s)	-	-
Protease	0.058	0.072	0.041	0.033	0.052	0.013
Amylase	0.01	0.03	0.012	0.007	0.016	0.002
Lipase	0.005	-	-	-	-	-
PB1	1.6	7.7	12.2	10.6	15.7	-
PB4	6.9	-	-	-	-	14.4
Nonionic	1.5	2.0	1.5	1.65	0.8	6.3
PAAC	-	-	0.02	0.009	-	-
MnTACN	-	-	-	-	0.007	-
TAED	4.3	2.5	-	-	1.3	1.8
HEDP	0.7	-	-	0.7	-	0.4
DTPMP	0.65	-	-	-	-	-
Paraffin	0.4	0.5	0.5	0.55	-	-
BTA	0.2	0.3	0.3	0.3	-	-
PA30	3.2	-	-	-	-	-
MA/AA	-	-	-	-	4.5	0.55
Perfume	-	-	0.05	0.05	0.2	0.2
Sulphate	24.0	13.0	2.3	-	10.7	3.4
Weight of tablet	25g	25g	20g	30g	18g	20g
pH	10.6	10.6	10.7	10.7	10.9	11.2
Miscellaneous and water	Up to 100%					

Example 18

# EP 0 971 021 A1

**[0145]** The following liquid dishwashing detergent compositions of density 1.40Kg/L were prepared according to the present invention :

	BO	BP	BQ	BR
STPP	17.5	17.5	17.2	16.0
Carbonate	2.0	-	2.4	-
Silicate	5.3	6.1	14.6	15.7
NaOCl	1.15	1.15	1.15	1.25
Polygen/carbopol	1.1	1.0	1.1	1.25
Nonionic	-	-	0.1	-
NaBz	0.75	0.75	-	-
PARP3	4.0(c)	2.0(c)	1.0(c)	0.5(c)
NaOH	-	1.9	-	3.5
KOH	2.8	3.5	3.0	-
pH	11.0	11.7	10.9	11.0
Sulphate, miscellaneous and water	up to 100%			

## Example 19

**[0146]** The following liquid rinse aid compositions were prepared according to the present invention :

	BS	BT	BU
Nonionic	12.0	-	14.5
Nonionic blend	-	64.0	-
Citric	3.2	-	6.5
HEDP	0.5	-	-
PEG	-	5.0	-
SCS	4.8	-	7.0
Ethanol	6.0	8.0	-
PARP5	6.0(c)	-	3.0(c)
PARP3	-	2.0(c)	1.0(c)
pH of the liquid	2.0	7.5	/
Miscellaneous and water	Up to 100%		

## Example 20

**[0147]** The following liquid dishwashing compositions were prepared according to the present invention :

	BV	BW	BX	BY	BZ
C17ES	28.5	27.4	19.2	34.1	34.1
Amine oxide	2.6	5.0	2.0	3.0	3.0
C12 glucose amide	-	-	6.0	-	-
Betaine	0.9	-	-	2.0	2.0
Xylene sulfonate	2.0	4.0	-	2.0	-
Neodol C11E9	-	-	5.0	-	-
Polyhydroxy fatty acid amide	-	-	-	6.5	6.5
Sodium diethylene penta acetate (40%)	-	-	0.03	-	-
TAED	-	-	-	0.06	0.06

EP 0 971 021 A1

	BV	BW	BX	BY	BZ
Sucrose	-	-	-	1.5	1.5
Ethanol	4.0	5.5	5.5	9.1	9.1
Alkyl diphenyl oxide disulfonate	-	-	-	-	2.3
Ca formate	-	-	-	0.5	1.1
Ammonium citrate	0.06	0.1	-	-	-
Na chloride	-	1.0	-	-	-
Mg chloride	3.3	-	0.7	-	-
Ca chloride	-	-	0.4	-	-
Na sulfate	-	-	0.06	-	-
Mg sulfate	0.08	-	-	-	-
Mg hydroxide	-	-	-	2.2	2.2
Na hydroxide	-	-	-	1.1	1.1
Hydrogen peroxide	200ppm	0.16	0.006	-	-
PARP3	4.0(c)	-	2.0(c)	-	0.25(c)
PARP1	-	6.0(c)	-	4.0(s)	3(c)
Protease	0.017	0.005	.0035	0.003	0.002
Perfume	0.18	0.09	0.09	0.2	0.2
Water and minors	Up to 100%				

Example 21

[0148] The following liquid hard surface cleaning compositions were prepared according to the present invention :

	CA	CB	CD	CE	CF
PARP1	8.0(c)	-	6.0(s)	-	4.0(c)
PARP3	-	2.0(c)	-	1.0(c)	0.5(c)
Amylase	0.01	0.002	0.005	-	-
Protease	0.05	0.01	0.02	-	-
Hydrogen peroxide	-	-	-	6.0	6.8
Acetyl triethyl citrate	-	-	-	2.5	-
DTPA	-	-	-	0.2	-
Butyl hydroxy toluene	-	-	-	0.05	-
EDTA*	0.05	0.05	0.05	-	-
Citric / Citrate	2.9	2.9	2.9	1.0	-
LAS	0.5	0.5	0.5	-	-
C12 AS	0.5	0.5	0.5	-	-
C10AS	-	-	-	-	1.7
C12(E)S	0.5	0.5	0.5	-	-
C12,13 E6.5 nonionic	7.0	7.0	7.0	-	-
Neodol 23-6.5	-	-	-	12.0	-
Dobanol 23-3	-	-	-	-	1.5
Dobanol 91-10	-	-	-	-	1.6
C25AE1.8S	-	-	-	6.0	-
Na paraffin sulphonate	-	-	-	6.0	-
Perfume	1.0	1.0	1.0	0.5	0.2
Propanediol	-	-	-	1.5	-
Ethoxylated tetraethylene pentamine	-	-	-	1.0	-
2, Butyl octanol	-	-	-	-	0.5

**EP 0 971 021 A1**

	CA	CB	CD	CE	CF
Hexyl carbitol**	1.0	1.0	1.0	-	-
SCS	1.3	1.3	1.3	-	-
pH adjusted to	7-12	7-12	7-12	4	-
Miscellaneous and water	Up to 100%				

\*Na4 ethylenediamine diacetic acid

\*\*Diethylene glycol monohexyl ether

Example 22

[0149] The following spray composition for cleaning of hard surfaces and removing household mildew was prepared according to the present invention :

PARP3	4.0(c)
Amylase	0.01
Protease	0.01
Na octyl sulfate	2.0
Na dodecyl sulfate	4.0
Na hydroxide	0.8
Silicate	0.04
Butyl carbitol*	4.0
Perfume	0.35
Water/minors	up to 100%

\*Diethylene glycol monobutyl ether

Example 23

[0150] The following lavatory cleansing block compositions were prepared according to the present invention.

	CK	CL	CM
C16-18 fatty alcohol/50EO	70.0	-	-
LAS	-	-	80.0
Nonionic	-	1.0	-
Oleoamide surfactant	-	25.0	-
Partially esterified copolymer of vinylmethyl ether and maleic anhydride, viscosity 0.1-0.5	5.0	-	-
Polyethylene glycol MW 8000	-	38.0	-
Water-soluble K-polyacrylate MW 4000-8000	-	12.0	-
Water-soluble Na-copolymer of acrylamide (70%) and acrylic acid (30%) low MW	-	19.0	-
Na triphosphate	10.0	-	-
Carbonate	-	-	-
PARP5	8.0(c)	-	6.0(c)
PARP3	-	2.0(c)	0.5(c)
Dye	2.5	1.0	1.0
Perfume	3.0	-	7.0
KOH / HCL solution	pH 6-11		

# EP 0 971 021 A1

## Example 24

[0151] The following toilet bowl cleaning composition was prepared according to the present invention.

	CN	CO
C14-15 linear alcohol 7EO	2.0	10.0
Citric acid	10.0	5.0
PARP2	2.0(c)	-
PARP3	-	4.0(c)
DTPMP	-	1.0
Dye	2.0	1.0
Perfume	3.0	3.0
NaOH	pH 6-11	
Water and minors	Up to 100%	

## Example 25

[0152] The following fabric softening compositions are in accordance with the present invention

Component	CP	CQ	CR	CS	CT	CU
DTDMAC	-	-	-	-	4.5	15.0
DEQA	2.6	2.9	18.0	19.0	-	-
Fatty acid	0.3	-	1.0	-	-	-
HCl	0.02	0.02	0.02	0.02	0.02	0.02
PEG	-	-	0.6	0.6	-	0.6
Perfume	1.0	1.0	1.0	1.0	1.0	1.0
Silicone antifoam	0.01	0.01	0.01	0.01	0.01	0.01
PARP 3	4.5(c)	1.0(c)	3.0(s)	3.0(c)	1.0(s)	6.0(c)
Electrolyte (ppm)	-	-	600	1200	-	1200
Dye (ppm)	10	10	50	50	10	50
Water and minors to balance to 100%						

## Example 26

[0153] The following dryer added fabric conditioner compositions were prepared according to the present invention :

	CV	CW	CX	CY
DEQA(2)	-	-	-	50.0
DTMAMS	-	-	26.0	-
SDASA	70.0	70.0	42.0	35.0
Neodol 45-13	13.0	13.0	-	-
Ethanol	1.0	1.0	-	-
PARP 3(c)	1.5	-	1.5	3.0
PARP 3(s)	-	1.5	-	-
Perfume	0.75	0.75	1.0	1.5
Glycoperse S-20	-	-	-	10.0
Glycerol monostearate	-	-	26.0	-
Digeranyl Succinate	0.38	0.38	-	-



**EP 0 971 021 A1**

	CV	CW	CX	CY
Clay	-	-	3.0	-
Dye	0.01	0.01	-	-
Minors to balance to 100%				

**Claims**

1. A process for making particles of amine reaction product of a compound containing a primary amine functional group and an active ketone or aldehyde containing component, and which comprises the steps of:

- a)-providing an amine reaction product, and
- b)-mixing therewith a carrier having a melting point between 30°C and 135°C.

2. A process according to Claim 1, wherein said particle is treated to form a coated particle.

3. A process according to either one of Claim 1 or 2, wherein the amine reaction product has a viscosity of higher than 1000cps.

4. A process according to any one of Claims 1-3, wherein the primary amine is selected from aminoaryl derivatives, polyamines, amino acids and derivatives thereof, substituted amines and amides, glucamines, dendrimers, the polyvinylamines with a MW of from 600-50K; amino substituted polyvinylalcohol with a MW ranging from 400-300,000; polyoxyethylene bis [amine]; polyoxyethylene bis [6-aminoethyl]; N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched; 1,4-bis-(3-aminopropyl) piperazine, and mixtures thereof, preferably selected from ethyl-4-amino benzoate, polyethyleneimine polymers; glucamine; the diaminobutane dendrimers, polyvinylamines with a MW ranging from 600, 1200, 3K, 20K, 25K or 50K; amino substituted polyvinylalcohol with a MW ranging from 400-300,000; polyoxyethylene bis [amine]; polyoxyethylene bis [6-aminoethyl]; -N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched; 1,4-bis-(3-aminopropyl) piperazine, and mixture thereof, more preferably selected from ethyl-4-amino benzoate, polyethyleneimine polymers; the diaminobutane dendrimers, N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched; 1,4-bis-(3-aminopropyl) piperazine, and mixtures thereof, most preferably selected from ethyl-4-amino benzoate, polyethyleneimine polymers; N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched, 1,4-bis-(3-aminopropyl) piperazine, and mixtures thereof.

5. A process according to any one of Claims 1-4, wherein the active is a perfume.

6. A process according to any one of Claims 1-5, wherein the perfume is selected from alpha-damascone, delta damascone, Carvone, Gamma-Methyl-Ionone; Damascenone, hedione, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, Florhydral, Lilial, heliotropine, trans-2-nonenal, citral, and mixtures thereof.

7. A process according to any one of Claims 1-6, wherein the amount of amine reaction product ranges from 1 to 75%, preferably 5 to 30%, by weight of the processed amine reaction product.

8. A process according to any one of Claims 1-7, wherein the carrier has a melting point between 45°C and 85°C.

9. A process according to any one of Claims 1-8, wherein said carrier is selected from organic polymeric compounds, waxes, paraffins, oils, glycerides, monoglycerides, diglycerides, triglycerides, anionic surfactants; nonionic surfactants, cationic surfactants, zwitterionic surfactants, and mixtures thereof, preferably selected from organic polymeric compound, nonionic surfactants, and mixtures thereof, more preferably nonionic surfactants selected from nonionic ethoxylated alcohols.

10. A process according to any one of Claims 1-9, wherein the amount of carrier material ranges from 3 to 95%, preferably from 15 to 80% and most preferably from 25 to 75%, by weight of the produced particles of the processed amine reaction product.

11. A process according to any one of Claims 1-10, wherein the coating is made of water-soluble agglomerating agent.

12. A process according to Claim 11, wherein the water-soluble agglomerating agent is selected from water soluble organic polymeric compounds, water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, carbonates, bicarbonates, borates, phosphates, sulfate salts, inorganic perhydrate salts, silicates, starch, cyclodextrin, and mixtures thereof, preferably selected from starch, carbonate, cyclodextrin, and mixtures thereof.

**EP 0 971 021 A1**

**13 .** A process according to any one of Claims 1-12, wherein the amount of amine reaction product ranges from 1 to 75%, preferably 5 to 30%, by weight of the coated particle.

**14 .** A processed amine reaction product as obtainable by the process of Claims 1-13.

5      **15 .** A method of incorporating an amine reaction product according to Claim 14 into finished product.

**17 .** A finished composition comprising one or more laundry or cleaning ingredient and a processed amine reaction product according to Claim 14.

10      **18 .** A composition according to Claim 17, wherein said composition is selected from a laundry composition, hard surface cleaning composition, personal cleaning composition.

**19 .** A method for delivering residual fragrance to a surface which comprises the steps of contacting said surface with a processed product according to Claim 14, or composition according to either one of Claim 17 or 18, and thereafter contacting the treated surface with a material so that the perfume is released.

15      **20 .** Use of a product as defined in Claim 14 for the manufacture of a laundry and/or cleaning composition for delivering residual fragrance on a surface on which it is applied.

**21 .** Use of a product as defined in Claim 14 for the manufacture of a laundry and/or cleaning composition for delivering residual fragrance and fabric care onto the fabrics on which it is applied.

20      **22 .** A packaged composition comprising the processed product of Claim 14 or composition of either one of Claim 17 or 18.

25

30

35

40

45

50

55



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 99 87 0029

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 430 315 A (UNILEVER NV ; UNILEVER PLC (GB)) 5 June 1991 (1991-06-05) * page 3, line 19 - line 22 * * page 3, line 34 - line 37 * * claims 1,7-10; examples 2BC,3 *	1,5,14, 17,19-21	C11D3/00 C11D3/20 C11D3/30 C11D3/22 C11D3/37 C11D3/33 C11D3/50 C11D17/06
A	EP 0 831 143 A (PROCTER & GAMBLE) 25 March 1998 (1998-03-25) * synthesis examples V-VIII * * claims; example 4 *	1,3-9, 14-22	
A	US H1468 H (COSTA JILL B ET AL) 1 August 1995 (1995-08-01) * column 4, line 39 - line 41; claims 1,8; example II; table II *	1,5,8,9, 14,20,21	
A	WO 98 08925 A (CHAPMAN BENJAMIN EDGAR ; PROCTER & GAMBLE (US)) 5 March 1998 (1998-03-05)	1,11,12, 14-18	
A	EP 0 041 328 A (UNILEVER PLC ; UNILEVER NV (NL)) 9 December 1981 (1981-12-09) * claims *	1-22	TECHNICAL FIELDS SEARCHED (Int.Cl.7)  C11D
A	KAMOGAWA H ET AL: "Chemical release control- Schiff bases of perfume aldehydes and aminostyrenes" JOURNAL OF POLYMER SCIENCE, POLYMER CHEMISTRY EDITION, vol. 20, 1 January 1982 (1982-01-01), pages 3121-3129, XP002084908 ISSN: 0887-624X	1	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>26 October 1999</b>	Examiner <b>Loiselet-Taisne, S</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document	

EPO FORM 1503 03/92 (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 87 0029

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-10-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0430315 A	05-06-1991	AT 150079 T	15-03-1997
		AU 648039 B	14-04-1994
		AU 6319890 A	11-04-1991
		CA 2026512 A	30-03-1991
		DE 69030156 D	17-04-1997
		DE 69030156 T	19-06-1997
		DK 430315 T	22-09-1997
		ES 2098244 T	01-05-1997
		GR 3023401 T	29-08-1997
		JP 2529896 B	04-09-1996
		JP 3131696 A	05-06-1991
EP 0831143 A	25-03-1998	WO 9812236 A	26-03-1998
US H1468 H	01-08-1995	EP 0679714 A	02-11-1995
		JP 8053699 A	27-02-1996
WO 9808925 A	05-03-1998	EP 0922087 A	16-06-1999
		ZA 9707164 A	01-09-1998
EP 0041328 A	09-12-1981	AT 10507 T	15-12-1984
		AU 554020 B	07-08-1986
		AU 7058481 A	19-11-1981
		CA 1165693 A	17-04-1984
		JP 1509975 C	26-07-1989
		JP 57016972 A	28-01-1982
		JP 63052150 B	18-10-1988
		US 4511495 A	16-04-1985
		ZA 8103215 A	29-12-1982

EPO FORM P0469

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82